REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE

3. REPORT TYPE AND DATES COVERED
FINAL TECHNICAL 01 Aug 93 - 30 Sep 96

4. TITLE AND SUBTITLE
(AASERT-93) NEW MATERIALS FOR ELECTRONIC APPLICATIONS

5. FUNDING NUMBERS
61103D
3484/TS

6. AUTHOR(S)
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AFOSR-TR-96
0582

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NE
110 Duncan Avenue Suite B115
Bolling AFB DC 20332-8080

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
F49620-93-1-0482

11. SUPPLEMENTARY NOTES

19961223 022

12a. DISTRIBUTION/AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The objective of the project was the discovery of new materials which might be useful as superconducctors, useful in superconducting devices, or useful in other electronic applications. Some insulating cuprates have been converted to superconductors by intercalation with oxygen, e.g., La2CuO4 _x and YBa3Cu3O6 x. In these cases an insulator is converted to a p-type conductor. We tried the opposite approach, ie.e., cation intercalation to produce n-type conductors. Layered cuprates of the type A2CuO2 _x and A3Cu2O4X2 (A = Ca or Sr; X - Cl, Br) were the starting points. Lithium intercalation was attempted by reaction of these materials with n-butyl lithium. Although some intercalation appeared to occur, no superconductivity was observed in the products.

14. SUBJECT TERMS

DTIC QUALITY INSPECTED 4

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18

FINAL TECHNICAL REPORT
AUGUST 1, 1993 – SEPTEMBER 30, 1996

Contract F49620-93-1-0482
Air Force Office of Scientific Research

New Materials for Electronic Applications

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The objective of the project was the discovery of new materials which might be useful as superconductors, useful in superconducting devices, or useful in other electronic applications.

Some insulating cuprates have been converted to superconductors by intercalation with oxygen, e.g., La_2CuO_{4+x} and $YBa_3Cu_3O_{6+x}$. In these cases an insulator is converted to a p-type conductor. We tried the opposite approach, i.e., cation intercalation to produce n-type conductors. Layered cuprates of the type $A_2Cu_2O_{2+x}$ and $A_3Cu_2O_4X_2$ (A = Ca or Sr; X = Cl, Br) were the starting points. Lithium intercalation was attempted by reaction of these materials with n-butyl lithium. Although some intercalation appeared to occur, no superconductivity was observed in the products.

Phases of the type Li_xNbO_2 and Na_xNbO_2 are known to be superconducting for certain values of x. We conducted proton exchange reactions with Li_xNbO_2 to produce a series of $(Li,H)_xNbO_2$ materials. None of these materials was superconducting above 4.2 K.

Compounds of the type A_xWO_3 and A_xMoO_3 (A = Li, Na, K, Rb, Cs, Ca, Sr, and Ba) can be metallic and superconducting. Compounds of the type Ba_xNbO_3 and Sr_xNbO_3 are also known, but they are not superconducting. We found that phases of the type Ca_xNbO_3 had not been reported. We have prepared such compounds with x ranging from 0.6 to 0.95. Although these materials are reasonably good electrical conductors, the temperature dependence of conductivity is never metal like. Also, we did not observe superconductivity for any value of x. Superficially, Ca_xNbO_3 phases have a very simple cubic structure. However, close examination of our X-ray diffraction data reveals a large superstructure which changes as x changes. This suggests a mechanism for electron localization in this system where delocalized electron behavior might be expected. The Ca^{2+}

cations are in fact ordered leading in effect to a charge density wave in a lattice which otherwise would be simple cubic. This charge density wave likely creates a periodic potential which traps the 4d electrons of Nb.

We thoroughly investigated a report of superconductivity at 20 K in the Ba/Nb/O system. We concluded that the superconducting phase reported was actually essentially NbN. Details of this work are given in our last report.

Superconductivity at temperatures as high as 34 K have been observed in $(K,Ba)BiO_3$ phases with the perovskite structure. We have produced new mixed valent compounds of bismuth by ion exchanging $NaBiO_3{\cdot}nH_2O$ with Sr and Ba. This has led to perovskite phases such as $(Ba_{0.44}Bi^{3+}_{0.56})(Na_{0.34}Bi^{5+}_{0.66})O_{2.77}$. However, none of these new perovskite phases showed superconductivity above 4.2 K.

Much of our work during the last year of this project has been on materials with low dielectric constant that might be used a substrates or interlayers in superconducting devices. Some of this work was on thin films prepared by sputtering. Films of Sr_2MgWO_6, Ca_2MgWO_6, Sr_2AlNbO_6, Sr_2AlTaO_6, and Sr_2GaNbO_6 were prepared because all of these have a good lattice match to the cuprate superconductors. The substrate was either MgO or $LaAlO_3$. Both on- and off-axis conditions were studied. Texture was evaluated by X-ray diffraction, and the morphology of the films was characterized by SEM and AFM. The most promising films were of Sr_2GaTaO_6 and Sr_2AlTaO_6. Thus, films of YBCO were grown on top of these films; T_c's as high as 87 K were obtained in such films.

$LaAlO_3$ has good properties as a substrate for cuprate superconductors. However, it has problems due to a phase transition and related twinning. Above about 500°C, $LaAlO_3$ is cubic. Below this temperature, it is rhombohedral. If films are grown on $LaAlO_3$ above 500°C, this phase transition in $LaAlO_3$ can seriously damage the films. Even if films are grown below 500°C on $LaAlO_3$, there

is a problem due to the twinning which is directly caused by the phase transition. We have found that the phase transition in $LaAlO_3$ can be completely suppressed by substitution of Sr for La. Materials of the type $La_{1-2x}Sr_{2x}O_{3-x}$ were prepared for a wide range of x values. It was found that x must be about 0.36 to suppress the phase transition. The dielectric properties of these substituted $LaAlO_3$ phases have been measured and found to be essentially unchanged from those of $LaAlO_3$. Thus, $La_{0.64}Sr_{0.36}O_{2.82}$ is a promising new substrate material.

Attempts were also made to prepare phases of the type A_2MgMO_5F (A = Ca, Sr, or Ba; M = Nb or Ta). In the case of A = Ba, good results were obtained. These may be useful dielectric materials because the polarizability of F^- and less than that of O^{2-}.